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APPLICATION

Of

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and

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for

LETTERS PATENT

for

INFUSION OF DYE USING A PLASTICIZER

Title of the Invention

INFUSION OF DYE USING A PLASTICIZER

Field of the Invention

The invention relates to the infusion of dyes into the surface of an article formed of a plastic material using one or more substances each capable of plasticicizing the material. More particularly, it relates to treating the surface of an article formed of a plastic material with a solution comprising one or more solvents each aggressive to said material, one or more dyes, and one or more substances capable of plasticizing the material.

Background of the Invention

Attempts have been made to introduce dyes into articles formed of a plastic material. For optical articles such as lenses, a thermoplastic frequently employed is polycarbonate, which is a condensation product resulting typically from the reaction of bisphenol A derivatives with phosgene. Many dyes degrade at the high molding temperature of polycarbonate. Accordingly it would be advantageous to treat the plastic article after it has been formed.

U.S. Patent 4,657,345 to Gordon utilizes aggressive solvents in combination with various heating steps. However, such surface defects as bubbling, hazing and crazing are caused by retained solvent. U.S. Patent 5,453,100 to Sieloff combines an aggressive solvent with a moderating solvent which acts to dilute and reduce the aggressiveness of the infusing solvent. This approach decreases the volatility of the solvent making it more difficult to drive off, resulting in increased bubble formation at or near the surface of the article. A variant of this approach is to utilize only non-aggressive solvents which reduces

solvent penetration and compromises dye density, for example, U.S. Patent 4,043,637 to Hovey, and U.S. Patent 4,323,597 to Olson.

Summary of the Invention

Our invention comprises treating the surface of a previously formed article of plastic material with one or more solvents aggressive to the plastic material having one or more dyes dissolved in the solvent and having further dissolved in the solvent one or more substances capable of plasticizing the material. It is preferable that the material have no plasticizer in it prior to formation of the article, since such would reduce the rigidity, strength and the mechanical properties of the formed article. The aggressive solvent enables penetration to depths in excess of 100 microns to achieve excellent dye density. The plasticizer is thought to provide sufficient polymer mobility to allow the solvent to almost completely escape during subsequent heating without causing bubbling, hazing or crazing. The extent of degradation of mechanical surface properties of the plastic article caused by retained plasticizer is negligible. It is the object of our invention to prevent bubbling and hazing of the surface of an article formed of a plastic material into the surface of which has been infused one or more dyes dissolved in one or more solvents each aggressive to the plastic by also dissolving in the solution one or more substances each capable of plasticizing the plastic material.

Description of the Preferred Embodiments

In the manufacture of optical devices, such as lenses, various dyes may be incorporated therein to affect the optical transmission characteristics. These dyes may include photochromic dyes, cosmetic tinting dyes, infrared absorbing dyes, laser radiation absorbing dyes and ultraviolet absorbing dyes. A combination of dyes may also be employed, for example, an ultraviolet absorbing dye to prevent

premature deterioration of a photochromic dye. Suitable photochromic dyes include palatinate purple, sea green, corn yellow and berry red which may be obtained from James Robinson, Ltd. of Huddersfield, United Kingdom.

A solvent aggressive to the plastic and also capable of dissolving the dye and a plasticizer is selected. An aggressive solvent is one which has a solubility parameter δ which, according to the theorem of Hildebrand, is within plus or minus 1 of the solubility parameter of the plastic when measured in $(cal/cm^3)^{0.5}$. Polycarbonate for example has a solubility parameter δ of 9.8 $(cal/cm^3)^{0.5}$. Suitable aggressive solvents for polycarbonate are tetrahydrofuran (C_4H_8O, δ = 9.1) and chlorinated hydrocarbons, for example, chloroform ($CHCl_3$, δ = 9.3), methylene chloride (CH_2Cl_2, δ = 9.7) and dichlorobenzene ($C_6H_4Cl_2$, δ = 10.0). The aggressive nature of the solvent allows the dye to penetrate to a sufficient depth of 75 to 150 microns below the surface of the article, enabling good dye density. A combination of aggressive solvents may be used. The use of non-aggressive solvents is disadvantageous because they do not provide sufficient dye penetration and further may be difficult to drive off. Although acetone has a solubility parameter of 9.9, its use should be avoided, since it is too volatile and causes crystallization of polycarbonate. Further, dodecanol-1, having a solubility parameter of 9.8, is not recommended because even higher alcohols are somewhat hydrophilic and tend to absorb water vapor.

Plasticizers are sometimes used during manufacturing to give an otherwise rigid plastic flexibility; but as previously indicated we prefer that the plastic have no plasticizer prior to formation of the article. In the present application, the infused plasticizer provides local surface mobility to the plastic matrix, allowing the deeply penetrating solvent to almost completely evaporate during subsequent heating. Where the plastic is polycarbonate, the plasticizer may be selected from the following table which includes both acid and alcohol moieties.

Table 1 - Listing of Acceptable Plasticizers

Trade Name	Chemical Name	Chemical Formula
Benzoflex(R) P-200	Polyethyleneglycol dibenzoate	$(C_2H_4O)_4C_{14}H_{10}O_3$
Benzoflex(R) S-552	Pentaerythritol tetrabenzoate	$C_{33}H_{28}O_8$
DOP	Dioctyl phtalate 98%	C_6H_4-1,2-$(CO_2CH_3)_2$
DPP	Dipropyl phthalate 99%	C_6H_4-1,2-$(CO_2\,CH_2\,CH_2CH_3)_2$
DMP	Dimethyl phthalate 99%	C_6H_4-1,2-$[CO_2CH_2CH(C_2H_5)(CH_2)\,CH_3]_2$
DOA	Dioctyl Adipate 99%	$C_{22}H_{42}O_4$
DOS	Dioctyl Sebacate 99%	$[-CH_2CH_2CO_2CH_2CH(C_2H_5)(CH_2)_3]_2$

One or more of these plasticizers may be used in combination. The plasticizers sold under the trademark BENZOFLEX(R) may be obtained from Velsicol Chemical Corporation of Rosemont, Illinois.

The treating solution comprises the aggressive solvent or solvents, typically 1% to 4%, or more, by weight of plasticizer dissolved in the solvent and a conventional quantity of dye dissolved in the solvent. As a general rule, it is preferable to use the minimum concentration of plasticizer necessary to achieve the desired result. The polycarbonate article is contacted with the solution for at least ten seconds, but generally not more than one minute. In the case of a lens, one or both surfaces of the lens may be coated with the solution or the lens may be completely immersed in the solution. In the case of immersion, the article is removed from the solution at a uniform withdrawal rate. The solvent is then evaporated from the surface layer of the article by annealing. In practice, annealing consisted of heating the article from 85^{0}F to 265^{0}F in four hours and then cooling the article from 265^{0}F to 85^{0}F in one hour. It will be appreciated that the maximum temperature is appreciably less than the glass transition temperature of polycarbonate of 305^{0}F. = 152^{0}C.

The resulting dyed article is transparent, having a surface layer with a depth of the order of 75 to 150 microns, which contains the infused dye and

plasticizer and, likely, trace amounts of retained solvent, which in larger amounts would cause bubbling, hazing or crazing.

When polycarbonate lenses were contacted with chloroform containing no plasticizer, the lenses became hazy and developed bubbles after annealing.

A lens contacted with chloroform containing 1% of either of the BENZOFLEX(R) plasticicizers had some bubbling and hazing after annealing. Increasing the concentration of plasticizer to 4% provided undetectable bubbling and haze after annealing. The remaining plasticizers caused no haze at 1% concentrations and no bubbling at 4% concentrations. The results of tests appear in the following table. It will be understood that a 4% plasticizer concentration may be achieved by combining any four of the above plasticizers in 1% concentrations each.

Plasticizer Trade Name	C ncentration	Bubbles after annealing	Haze
Control	No plasticizer	Yes	Yes
P-200	1%	Reduced in size	Reduced
	2%	Same	Same
	3%	Slightly less	Same
	4%	None	None
S-552 Solid	1%	Reduced	Greatly reduced
	2%	More reduced	Same
	3%	Same	Reduced
	4%	None	None
DOP 98%	1%	Reduced	None
	2%	More reduced	None
	3%	More reduced	None
	4%	None	None
DPP 99%	1%	Greatly reduced	None
	2%	Reduced	None
	3%	Reduced	None
	4%	None	None
DMP 99%	1%	Greatly reduced	None
	2%	Reduced	None
	3%	Same	None
	4%	None	None
DOA 99%	1%	Reduced	None
	5%	None	None
	8%	None	None
DOS 99%	1%	Reduced	None
	2%	None	None
	3%	None	None
	4%	None	None

Plastics other than polycarbonate would include polymethyl methacrylate (PMMA), $\delta = 9.09$, and polycarbonate-polyester copolymers (LEXAN), for which the foregoing solvents and plasticizers would be suitable, polystyrene (PS), $\delta = 8.56$, for which carbon tetrachloride, $\delta = 8.6$, methyl isopropyl ketone, $\delta = 8.5$, and propyl propionate, $\delta = 8.5$, would be suitable solvents and for which the foregoing phthalate plasticizers would be suitable, and polyethylene terephthalate (PET), $\delta = 9.5$, for which chlorobenzene, $\delta = 9.5$, and chlorostyrene, $\delta = 9.5$, would be suitable solvents and for which the foregoing phthalate plasticizers would be suitable. The glass transition temperature of polycarbonate is roughly 152°C., while that of PMMA is 105° C., that of PS is 100° C., and that of PET is 80° C. Of these thermoplastics, polycarbonate is the one for which our invention is especially useful, since for the other thermoplastics, there would be reduced dye degradation at the lower molding temperatures. It will further be understood that the maximum annealing temperature in each instance would be reduced to appreciably less than the glass transition temperature.

It will be seen that we have accomplished the object of our invention. We have prevented bubbling and hazing of the surface of an article formed of a plastic material into which has been infused a dye dissolved in a solvent aggressive to the plastic. This advantageous result is achieved by also dissolving in the solvent one or more substances each capable of plasticizing the material.

It will be understood that certain features and subcombinations are of utility and may be employed without reference to other features and subcombinations. This is contemplated by and is within the scope of our claims. It is further obvious that various changes may be made in details within the scope of our claims without departing from the spirit of our invention. It is, therefore, to be understood that our invention is not to be limited to the specific details shown and described.

Having thus described our invention, what we claim is: